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GENERATION OF CYANOGEN FROM THE DECOMPOSITION OF
SEVERAL NITROGEN CONTAINING AROMATICS ON PT(111)(U)
CALIFORNIA UNIV IRVINE DEPT OF CHEMISTRY

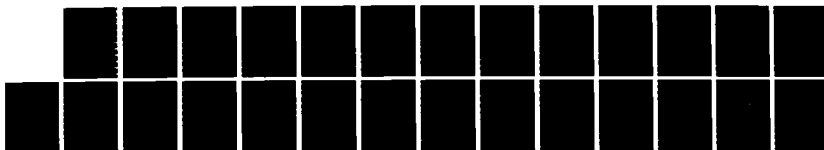
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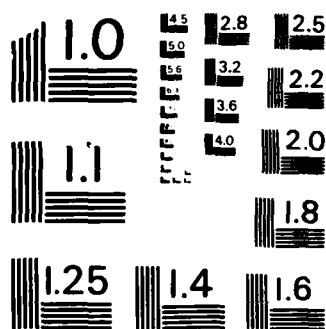
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GENERATION OF CYANOGEN FROM THE DECOMPOSITION OF
SEVERAL NITROGEN CONTAINING AROMATICS ON Pt(111)

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ABSTRACT

The thermal decomposition of several nitrogen containing aromatics on Pt(111) results in desorption products of H_2 , HCN and C_2N_2 . C_2N_2 from triazine decomposition desorbs at 740 K which is the same temperature for C_2N_2 desorption following adsorption of cyanogen. All of the other aromatics evolve C_2N_2 at a significantly higher temperature (830-990 K) which corresponds to the onset of decomposition of the dehydrogenated aromatic ring. The similar temperature for C_2N_2 production from triazine and cyanogen indicates that a macrocyclic model of the β state of cyanogen adsorbed on Pt(111) which has been previously suggested is likely.

^a Alfred P. Sloan Research Fellow

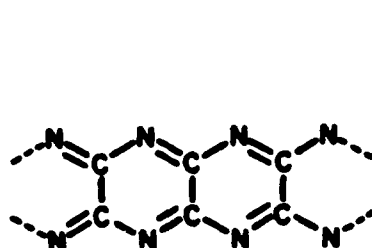
1. Introduction

Recently there have been several studies of the bonding and chemistry of nitrogen containing molecules on the surfaces of a variety of single crystal metals. CH_3CN [1], CH_3NC [1], HCN [2,3], C_2N_2 [1,2,4-10], $\text{C}_2\text{H}_8\text{N}_2$ [12], and $\text{C}_4\text{N}_4\text{H}_6$ [11] have been the objects of studies on various surfaces of Pt, Ni, and Cu.

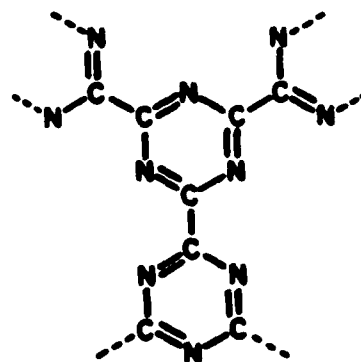
The thermal chemistry of C_2N_2 has been studied previously on Pt(100) [5,9,10], Pt(110) [2,6], Pt(111) [8,12] and a stepped Pt surface with Pt(111) terraces [7]. Only C_2N_2 is observed as a desorption product from these surfaces (see fig. 1 as an example of cyanogen desorption from Pt(111)). In all of these cases at least two desorption states are seen (designated α and β_1). On several of these surfaces a second β state is seen and designated β_2 . The α state desorbs in the temperature range of 370 K (for Pt(111)) to 460 K (for Pt(110)). The β_1 state desorbs in the range 680-690 K. The β_2 state desorbs in the range 750 K to above 800 K. The present interpretation of the α state is that it is due to molecularly adsorbed cyanogen. Two interpretations of the β states have been put forward. Bridge, Marbrow and Lambert [2] have suggested that the β states are due to a recombination of CN groups, while Netzer [5] has proposed the existence of a paracyanogen-like overlayer. Similar high temperature states are observed for cyanogen adsorption on other transition metal surfaces such as Ni(111) [1].

Two suggestions have appeared in the literature for possible

$(CN)_{2x}$ polymeric structures for the β states of cyanogen on transition metals [1,5]. The paracyanogen-like structure (1) has been suggested by Netzer et. al. while Hemminger et. al. have suggested the existence of a cyanogen trimer on Ni(111) which may be extended into a macrocyclic structure (2).



(1)



(2)

In an effort to develop an understanding of the chemistry which should be expected for species like (1) and (2) we have studied the thermal chemistry of a number of nitrogen containing aromatic molecules which decompose at high temperatures to give cyanogen when adsorbed on Pt(111) (see fig. 6 for the names and structures of the molecules studied in this report).

The decomposition chemistry of triazine may be expected to be similar to that of macrocycle (2) whereas quinoxaline chemistry would be expected to be close to that of the paracyanogen structure (1). As we will see the cyanogen evolution from triazine is unique among the molecular adsorbates we have studied. The other chemical analogs to quinoxaline and triazine in this study will act as a check as to the uniqueness of the

thermal chemistry of triazine.

2. Experimental

All experiments were performed in a UHV chamber equipped with Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES) and a quadrupole mass spectrometer in conjunction with a custom built data system, all of which have been described elsewhere [12]. In thermal desorption experiments up to 16 masses can be monitored simultaneously.

All gas exposures were performed in the pressure range of 1×10^{-9} to 5×10^{-7} torr. Pressures were read directly from the ion gauge without correction for sensitivity relative to N_2 . All reagents were purchased from Aldrich Chemical Co. All reagents were used without further purification with the exception of quinoxaline. The quinoxaline showed signs of oxidation and was vacuum sublimed at room temperature to obtain a pure sample. The piperazine was handled under an inert atmosphere to avoid air contamination. All reagents were introduced into the vacuum chamber from a stainless steel gas manifold through sapphire-sealed leak valves. If necessary, the manifold was heated to raise the vapor pressure of the reagent being used. After exposures were made, the system was allowed to pump for as long as an hour to reduce the background of each reagent, as all are very 'sticky' molecules.

3. Results

3.1 Quinoxaline on Pt(111)

Exposures of quinoxaline were made at 283 K. After adsorption no evidence was observed for ordering of the overlayer either before or after slow warming of the crystal.

Figure 2 shows typical thermal desorption spectra (TDS) of H_2 , HCN and C_2N_2 following a 1 Langmuir (L) exposure of quinoxaline. The single cyanogen desorption peak at 960 K occurs at a much higher temperature than any cyanogen desorption previously observed from a Pt surface. Confirmation that the observed cyanogen desorption was coming from the crystal and not from the heating wires or other source was obtained by monitoring the nitrogen Auger signal from the surface. This desorption peak, along with those for H_2 and HCN, do not show any temperature dependence on exposure.

3.2 Triazine on Pt(111)

Figure 3 shows typical desorption spectra for H_2 , HCN and C_2N_2 following exposure of 2 L of triazine at 273 K. The peak temperatures for all three products showed no exposure dependence. No evidence of ordering of the adsorbate was seen at any exposure level or upon a slow heating.

Monitoring of the carbon and nitrogen Auger signals before and after desorption indicate that the triazine is completely removed from the surface with heating to 1300 K. The $C_{272}:N_{391}$ Auger signal ratio after exposure was found to be approximately 1:1. This ratio is higher than what would be expected (0.7) and may be indicative of some amount of electron beam damage to the triazine.

In several experiments with triazine, a second cyanogen peak was observed at 680 K. This second peak varied in size from run to run relative to the peak at 740 K. It was found that this state is the result of residual amounts of oxygen in the bulk of the Pt crystal left over from an oxygen cleaning. Figure 4 shows the results of an oxygen cleaning exposure at 873 K and 1×10^{-6} torr oxygen for 1 minute and subsequent adsorption of triazine. It should be noted that in this experiment the crystal was not flashed to high temperature after the oxygen treatment to remove residual oxygen as is typically done in cleaning of the crystal. As can be seen, residual oxygen causes total population of the 680 K peak. Subsequent exposures and desorptions from this crystal show a gradual shift of cyanogen population to the 740 K peak, leaving only a shoulder at 680 K. Careful cleaning and high temperature annealing of the crystal resulted in complete elimination of this shoulder. H_2 and HCN were relatively unaffected by residual dissolved oxygen. Similar effects of impurities has been observed for C_2N_2 adsorption [13].

Coadsorption of triazine with D_2 resulted in no

incorporation of deuterium into either the HCN or the high temperature H_2 peak.

Preadsorption of 5 L of cyanogen with 2 L of triazine had little effect on the HCN desorption spectrum. The cyanogen desorption spectrum showed an additional peak at 370 K, which is the same as is seen for simple desorption of just cyanogen on Pt(111) [8,12]. The hydrogen spectrum displayed a loss of the low-temperature background peak. This hydrogen was most likely bound up by the cyanogen on the surface at the time of adsorption and was removed in the higher temperature H_2 peak. This effect has been seen previously in cyanogen-hydrogen coadsorption experiments, where it is demonstrated that a partially hydrogenated surface species is created [12].

3.3 Pyridazine on Pt(111)

Exposures of pyridazine were made at 300 K. Again, no ordered structures were observed following adsorption on Pt(111). Figure 5 shows typical thermal desorption spectra (TDS) of H_2 , HCN and C_2N_2 following a 2 Langmuir exposure of pyridazine. As in the case of quinoxaline the C_2N_2 desorption peak is observed at a temperature (833 K) significantly above the B state for cyanogen adsorption on Pt(111). An interesting side note is that we did not observe nitrogen desorption following adsorption of pyridazine. This is in marked contrast with results for the

decomposition of dimethyltetrazine on Pt(111) which results in both low temperature N_2 production, indicative of direct release of molecular nitrogen during the decomposition, and a higher temperature N_2 product, indicative of N atom recombination [11].

3.4 Other Nitrogen Aromatics on Pt(111)

The results just described for quinoxaline and pyridazine decomposition on Pt(111) are characteristic of what we have observed for a variety of similar nitrogen containing aromatic analogs adsorbed on Pt(111). Figure 6 collects the results we have obtained for the decomposition of pyrimidine, pyrazine, piperazine, and quinazoline along with the results just described for pyridazine, quinoxaline, triazine and cyanogen. Figure 6 indicates the peak temperatures and relative abundances for the decomposition products H_2 , HCN and C_2N_2 . It is clearly seen that the molecules we have studied can be put into three classes: single ring compounds with two nitrogens; naphthalenic compounds with two nitrogens; and triazine. All of the single ring compounds have very similar decomposition behavior. Piperazine, the saturated analog of pyrazine, undergoes dehydrogenation at low temperatures (possibly upon adsorption). After the initial low temperature dehydrogenation the chemistry of piperazine is nearly identical to that of pyrazine. Quinoxaline and quinazoline show H_2 , HCN and C_2N_2 production at very similar temperatures.

Both of these classes of molecules result in C_2N_2 production at temperatures significantly above the B state observed for cyanogen adsorption on Pt(111). In contrast, triazine decomposes at a significantly lower temperature resulting in C_2N_2 production at 740 K. This is the same temperature as the B state of cyanogen.

4. Discussion

The high temperature at which cyanogen is released from quinoxaline and quinazoline adsorbed on Pt(111) suggests that the naphthalene-like ring structure of these compounds is extremely stable, even when it has been dehydrogenated. Loss of cyanogen is not the only method by which this stable ring structure is broken. As is seen in section 3.1 and 3.3, a significant amount of HCN is seen to evolve during the course of the experiment. The evolution of HCN occurs in direct competition with loss of hydrogen at around 700 K. When all of the hydrogen has been lost, ring cleavage is no longer favorable and the molecules which have not lost their -CN groups are stable up to 960 K where cyanogen is produced.

The stability of the aromatic backbone of quinoxaline and quinazoline is further evidenced by two additional experiments. First we have adsorbed quinoxaline on a Pt(111) surface with small amounts of residual oxygen in the crystal.

Under these conditions CO is produced and observed as a sharp peak in the TDS spectrum of mass 28 coincident with the cyanogen (960 K). Similar production of CO is observed when naphthalene is adsorbed on a partially oxidized Pt(111) surface. In the naphthalene case the CO is observed at a temperature of 925 K. Thus we believe that the high temperature cyanogen from quinoxaline is produced at a temperature which is characteristic of the decomposition of the naphthalene like aromatic ring structure which has been completely dehydrogenated at temperatures below 800 K (see fig. 2 for the temperature of hydrogen evolution). After decomposition of the aromatic ring the carbon residue which is left behind forms graphite islands, as evidenced by observation of rings in the LEED pattern characteristic of graphite overlayers.

Another indication of the stability of the quinoxaline backbone is the high temperature at which HCN is evolved. Both triazine and the adsorption of HCN directly on Pt(111) give HCN desorption at a temperature of 510 K [3]. This is also true of HCN production from dimethyltetrazine [11]. This is in contrast to the higher temperature (740 K) required to produce HCN from quinoxaline and quinazoline.

If Netzer's suggestion of a paracyanogen-like overlayer (1) is correct, one would envision chemistry similar to that of the cyanogen group in quinoxaline. That being the case, one would expect that the desorption temperature for cyanogen from such a structure might resemble that for quinoxaline. This is not what

is observed. As was mentioned in the introduction, the B desorption state of cyanogen from Pt(111) is observed at 680 K.

Similar behavior has been observed for the single ring compounds which contain only two nitrogens. The decomposition of the ring structure is first indicated by HCN production at temperatures above 625 K and C_2N_2 is not observed until temperatures above 830 K (well above the temperature of the cyanogen B state). Both of these classes of molecules are in direct contrast to triazine.

The molecule triazine provides a model of the repeating unit of the macrocyclic model (2) for the B state of cyanogen in which the hydrogens replace the connecting bonds to other units. The bonding in triazine and the macrocycle shown earlier is such that formation of cyanogen must result from either decomposition to isolated $-CN$ followed by recombination or a concerted formation of cyanogen involving $-CN$ groups from different triazine-like units. Our results with triazine show that cyanogen is observed at the same temperature as the B state produced by cyanogen adsorption.

The desorption spectra following triazine exposure suggests a relatively simple picture of the thermal chemistry of triazine on Pt. Triazine is thought to be molecularly adsorbed on Pt(111) at room temperature. Upon heating, two hydrogen atoms are removed at 485 K. At slightly higher temperatures a molecule of HCN is split out of the aromatic ring. Finally at 740 K, cyanogen is desorbed at the same temperature as the B state of cyanogen.

5. Summary

The production of C_2N_2 from the naphthalene like molecules quinoxaline and quinazoline as well as from the single ring compounds with two nitrogens occurs at temperatures significantly above the temperature of the cyanogen B state. Of the nitrogen containing molecules which we have studied on Pt(111) only triazine results in C_2N_2 desorption at a temperature similar to that of the cyanogen B state.

We interpret the evolution of cyanogen from quinoxaline and quinazoline at 960 K as the onset of fragmentation of the naphthalene-like aromatic ring structure after complete dehydrogenation. The extremely high desorption temperature (960 K) of cyanogen observed from quinoxaline adsorbed on Pt(111) suggests that the paracyanogen (i) model for the B state of cyanogen on Pt(111) is unlikely. On the other hand, the desorption temperature of cyanogen from triazine (similar structurally to the macrocyclic model for the B state) is identical to that of the B state. It is however possible that this is still due to the recombination of isolated -CN groups formed after initial release of HCN. Study of these systems by surface spectroscopic probes will be necessary to develop a clearer picture of the cyanogen B state.

Acknowledgement:

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FIGURE CAPTIONS

Figure 1. Typical TDS spectrum of cyanogen (mass 52) following adsorption of 20 L of cyanogen at 286 K on a Pt(111) crystal. Heating rate was 8 K/s.

Figure 2. H_2 , HCN and C_2N_2 TDS spectra after adsorption of 1 L of quinoxaline at 293 K on Pt(111). Heating rate was 8 K/s.

Figure 3. H_2 , HCN and C_2N_2 TDS spectra after adsorption of 1 L of triazine at 273 K on Pt(111). Heating rate was 8 K/s.

Figure 4. The effect of strongly bonded oxygen on the TDS spectrum of cyanogen after adsorption of 2 L of triazine at 273 K on Pt(111). (A) adsorption on clean surface. (B) crystal heated to 873 K for 1 minute in 1×10^{-6} torr O_2 before adsorption of triazine. (C) subsequent run after crystal had been flashed once to 800 K. Trace (C) has been enlarged slightly so as to not obscure trace (A). Heating rate was 8 K/s.

Figure 5. H_2 , HCN and C_2N_2 TDS spectra after adsorption of 2 L of pyridazine at 300 K on Pt(111). Heating rate was 8 K/s.

Figure 6. Desorption temperature and relative abundance for H_2 , HCN and C_2N_2 for each of the molecules in this study. Relative abundances are indicated by the height of the bar and are not

corrected for sensitivity and transmission factors. The relative amounts are normalized to the largest peak for each molecule but not to each other.

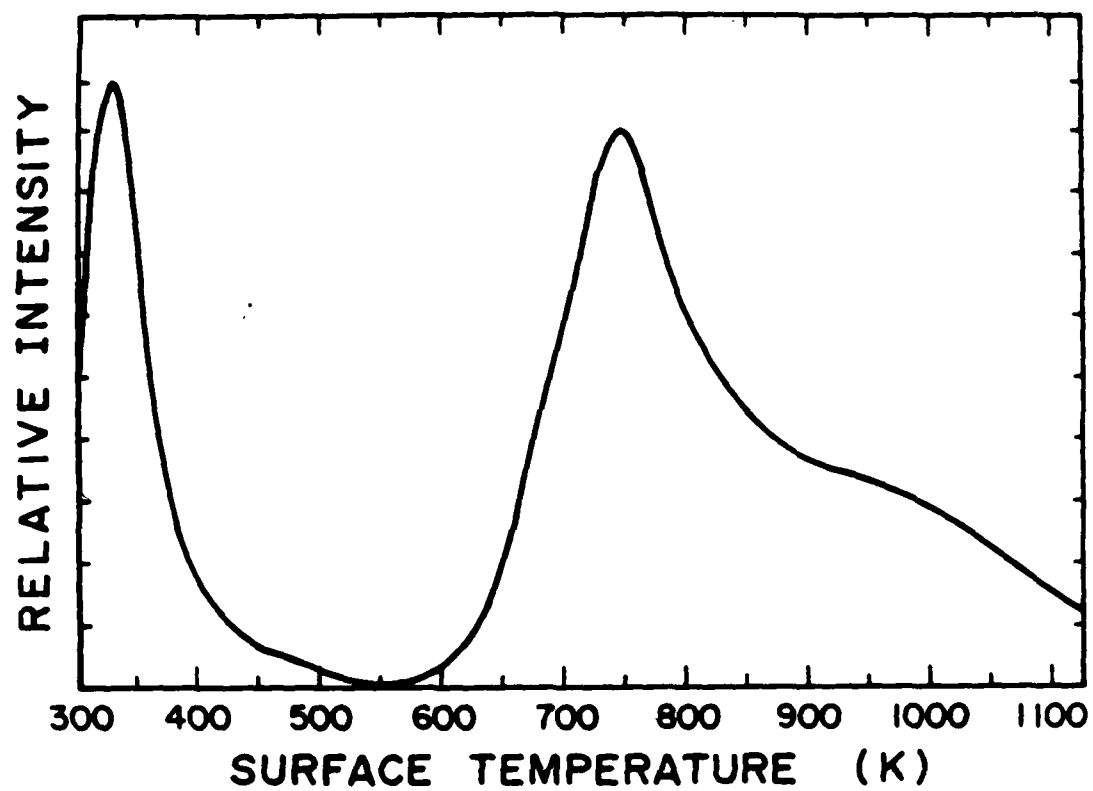


Fig. 1

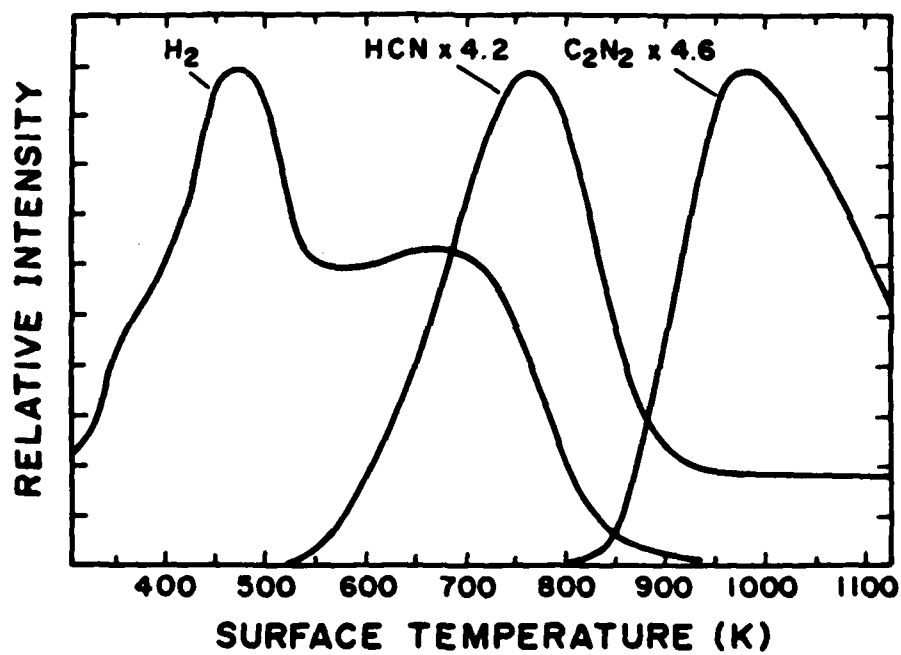


Fig. 2

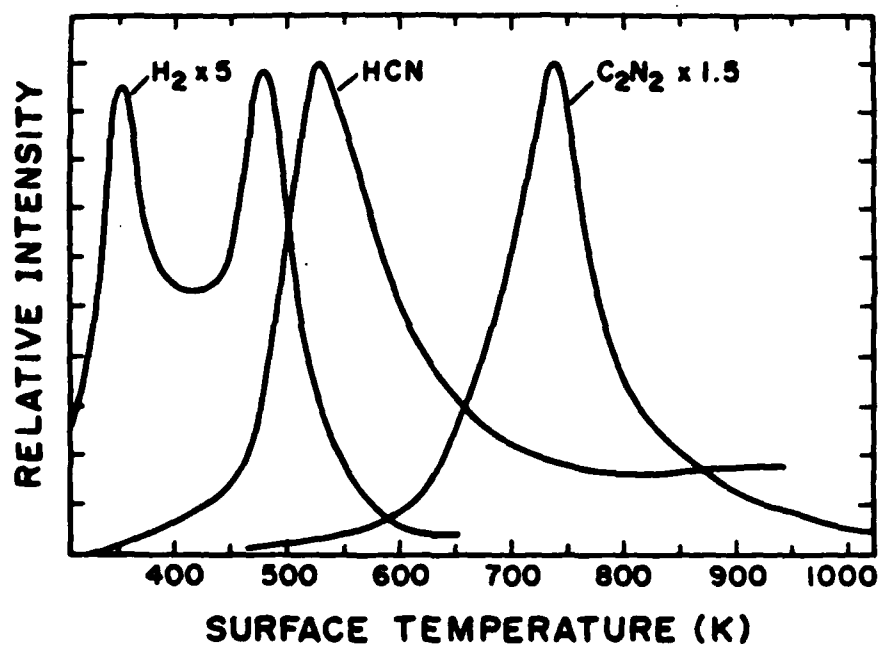


Fig. 3

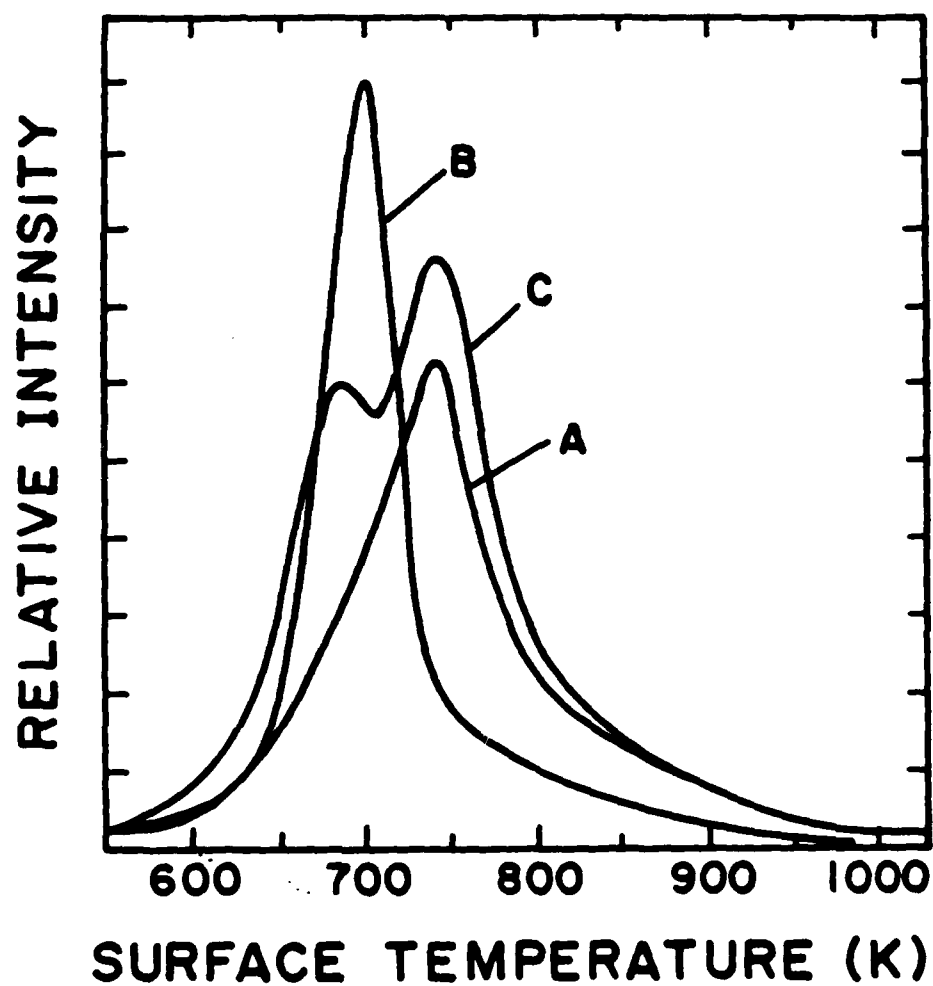


Fig. 4

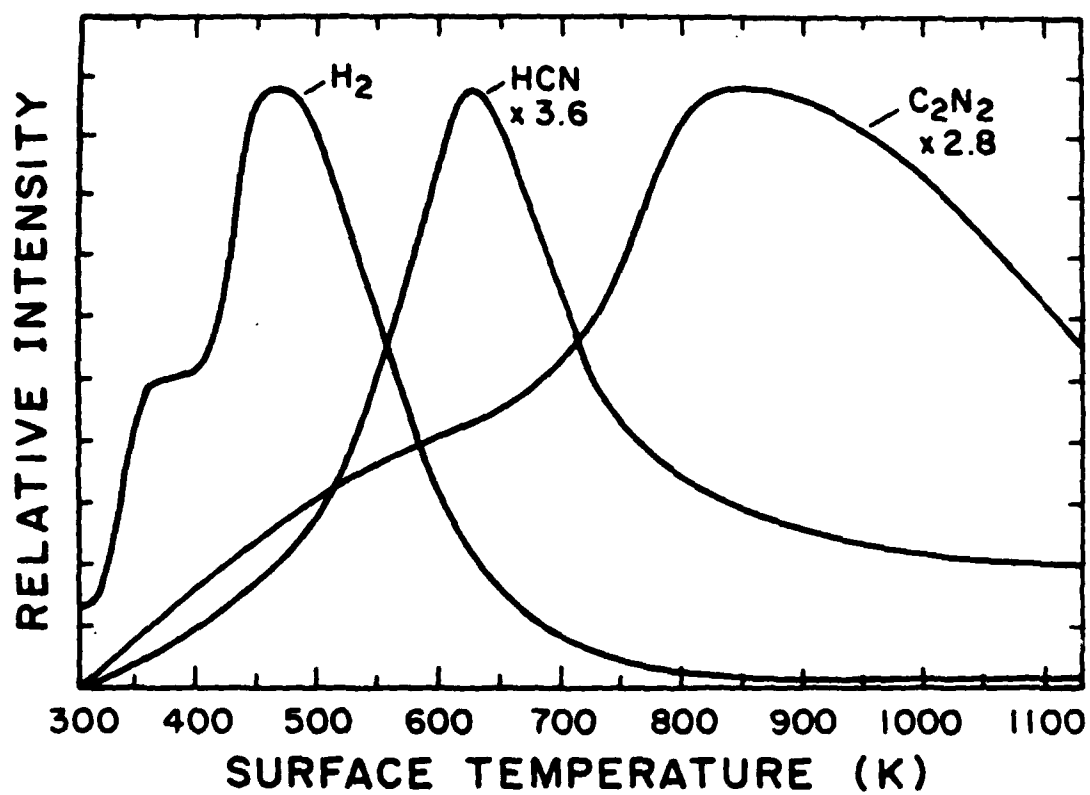
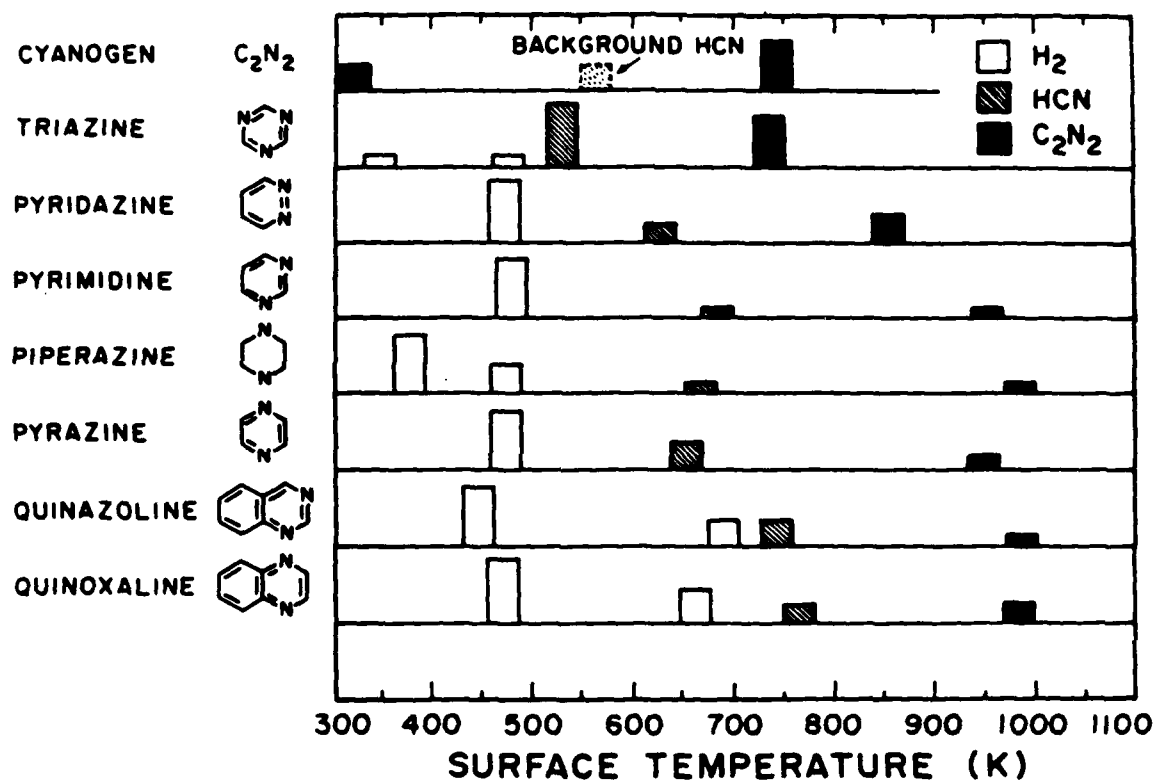


Fig. 5.



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